Collaborative Research: A Polymer Synthesis/Membrane Characterization Program on Fouling-Resistant Membranes for Water Purification.

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ABSTRACT: A novel reverse osmosis (RO) concentrate treatment process was developed; the goals of the treatment process are to remove problematic sparingly soluble salts that precipitate on the membrane surfaces and to increase the overall recovery of the RO process. The concentrate treatment process consists of three stages, including (I) antiscalant degradation, (II) salt precipitation, and (III) solid/liquid separation. Experiments were performed on a natural water sample from a karstic spring located near Marseille, France. Results were obtained for dissolved ion concentrations, precipitate particle size distribution, microfiltration flux, and orthophosphate produced. The effect of antiscalants on salt precipitation and microfiltration was evaluated, as well as the effect of antiscalant oxidation (through ozonation) on precipitation and filtration.

INTRODUCTION

An IREE grant was funded under the original NSF grant entitled "Collaborative Research: A Polymer Synthesis/Membrane Characterization Program on Fouling-Resistant Membranes for Water Purification" (PI: Benny D. Freeman at the University of Texas at Austin, Todd Emrick at the University of Massachusetts-Amherst, NSF grant #: CBET 0637040). The IREE supplement was used to send one Ph.D. student from UT-Austin, Ms. Lauren Greenlee, to the Universite Paul Cezanne in Marseille, France, to study a treatment process to reduce the volume of the waste stream produced during reverse osmosis membrane desalination. Ms. Greenlee was selected based on her communication skills, her interest in conducting research internationally, and the opportunity for her to extend her research to real water samples, pilot-scale membrane test facilities, and new analytical techniques.

The main objective of the current NSF grant is to enhance water purification membrane performance when filtering wastewaters with common conaminants (namely proteins and stable emulsified oil droplets). To accomplish this goal, commercial membranes are coated with an ultra-thin, nonporous, hydrophilic polymer that acts as a water-selective barrier. This coating layer rejects most contaminants and, due to its hydrophilic nature compared to the commercial membrane, dramatically reduces organic adhesion to the membrane. Therefore, the coating layer can simultaneously increase water flux and organic rejection in membrane systems. Most of our laboratory's initial work has focused on producing a coated membrane that is optimized with respect to oil-water emulsion purification.

The current NSF award focuses on membrane development for water treatment, including both reverse osmosis and ultrafiltration membranes. While the U.S. has many researchers working in the field of water treatment and membrane development, several other countries, including France and South Korea, also have leading research programs. Collaborations between the U.S. and these two countries could help advance the research field by allowing researchers to share ideas and experimental techniques. In addition, new and future collaborations depend on young researchers being able to be involved with international research collaborations. When the IREE program was started, it was the perfect opportunity to expand our water research project and to provide graduate students with international research experience during their doctorate degrees. Under the IREE program and the current NSF award, two students conducted research abroad, one in France and one in South Korea.

This report focuses on research conducted in France by Ms. Greenlee from August 2007 to August 2008. The host laboratory was the Laboratoire de Procédés Propres et Environnement (LPPE) (Laboratory of Clean and Environmental Processes) in Aix en Provence, France, at the Université Aix-Marseille III. This laboratory specializes in water and wastewater treatment processes, including drinking water treatment, desalination, biological treatment of wastewater, and membrane treatment processes. The laboratory has several laboratory- to pilot-scale membrane pilots, where full-size membrane modules can be tested under a variety of experimental conditions. The laboratory also has equipment and facilities for small-scale experiments and analytical measurements.

Ms. Greenlee's research project focuses on the development of a 3-stage process to treat the waste water (concentrate) stream that is produced during reverse osmosis membrane treatment of salt water to make drinking water. During her stay in France, she taught several courses in French at the Université Aix-Marseille III, including undergraduate chemical engineering laboratory courses and an English class. She also took a course on membranes at the university. She prepared and submitted a review on membrane desalination entitled "Reverse Osmosis Desalination: Water Sources, Technology, and Today's Challenges" and supervised the research project of a Master's student over 6 months. Her laboratory work focused on one part of her research project; she completed salt precipitation experiments, performed tests on real water samples, and used the membrane pilots to test the concentrate treatment process. This international experience has allowed additional laboratory experience and expanded the doctoral research project to include tests on real water samples and membrane pilots. In addition, the teaching experience and language development will allow Ms. Greenlee to continue to develop international contacts and pursue her career goal of being a professor.

RESEARCH ACTIVITIES AND ACCOMPLISHMENTS OF THE INTERNATIONAL COOPERATION

Ms. Greenlee's research project focuses on the development of a novel 3-stage concentrate treatment process that uses (I) antiscalant degradation, (II) salt precipitation (pH 10.5), and (III) solid/liquid separation to remove problematic sparingly soluble salts from reverse osmosis (RO) concentrate. Salts such as calcium carbonate ($CaCO_3$) have relatively low solubility limits and will precipitate on the surface of the RO membranes during desalination. Synthetic chemicals called antiscalants are often used in RO desalination to help reduce or prevent salt precipitation, but the precipitation control of antiscalants is eventually overcome as the salt concentrations increase. To limit precipitation, the recovery of RO desalination (ratio of product volume to feed volume) must be limited, and a significant waste volume is produced (at least 10% for brackish water). The goal of the concentrate treatment process is to increase the overall RO recovery by removing the problematic precipitates from the concentrate and returning a large portion of the concentrate volume to the membrane system (without the problematic salts).

During this international research experience, the program of research included a detailed investigation into the precipitation stage (Stage II) of the proposed concentrate treatment process, as well as experiments with a natural salt water from a karstic spring located near Marseille, France. Experiments were performed to determine the effect of antiscalants on precipitation, and the effect of antiscalant degradation on the concentrate treatment process. Antiscalant degradation was achieved through oxidation by addition of ozone and hydrogen peroxide. To analyze the precipitation stage, a laser particle counter was used to evaluate changes in particle size distribution. Dissolved ion concentrations were measured before and after precipitation to calculate the extent of precipitation of calcium, magnesium, sulfate, and carbonate. Stage III, solid/liquid separation, was performed using a dead-end filtration system with microfiltration membranes (0.1 μm pore size). Flux data were recorded during filtration of the precipitated solutions.

The specific phosphonate antiscalant used in experiments in shown in Figure 1. When phosphonate-type antiscalants are ozonated, the primary oxidation product is orthophosphate (PO_4^{3-}). Orthophosphate was measured in solution after ozonation and used as a measurement of the extent of antiscalant degradation. Results, shown in Figure 1, show that antiscalant degradation increases with ozonation time. Other parameters tested included ozone dose (mg O_3 per mg dissolved organic carbon), molar ratio of H_2O_2/O_3, antiscalant type, water composition, and antiscalant concentration.

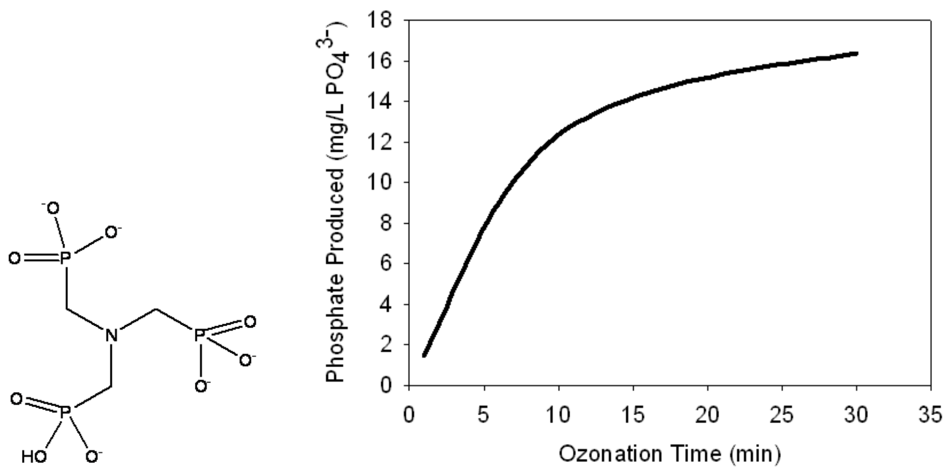

Figure 1. Molecular structure of the phosphonate antiscalant used in experiments (shown on left) and the effect of ozonation time on phosphonate antiscalant degradation. Initial phosphate contained in the antiscalant compound was 26 mg/L PO_4^{3-}.

The concentrate treatment process of antiscalant oxidation, precipitation, and solid/liquid separation (microfiltration) was performed on a natural water sample. Particle size measurements for this experiment, shown in Figure 2 on the left, indicated that the addition of antiscalant caused a decrease in the particle size distribution for a precipitated solution that did not have ozone treatment. When the sample was first treated with 10 minutes of ozone (3 mg/min ozone) and then precipitated, the particle size distribution increased and resembled the control experiment (the same precipitated water sample with no antiscalant or ozone). Therefore, ozonation of the antiscalant degrades and deactivates the antiscalant, removing the effect of the antiscalant on salt precipitation particle size. Results from subsequent filtration of the precipitated samples, shown in Figure 2 on the right, show that the addition of antiscalant causes a decrease in flux performance, and ozonation reduces the extent of flux decline. The control experiment (no antiscalant, no ozone) had the best flux performance and the smallest flux decline, indicating that ozonation does not completely remove the effect of the antiscalants on filtration performance. Ion concentration measurements (results not shown) indicate that ozonation increases calcium precipitation from approximately 80% to 87% (pH 10.5) for the water tested.

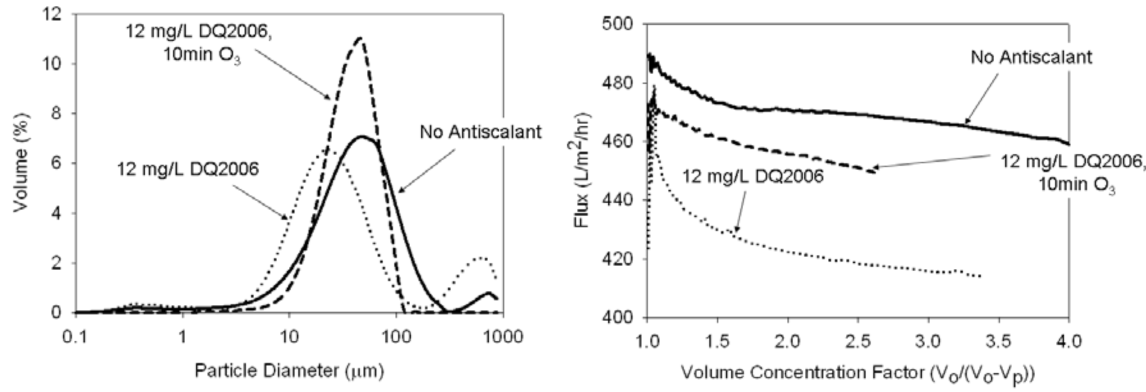

Figure 2. The effect of antiscalant ozonation on precipitate particle size (shown on left) and the effect of ozonation on microfiltration of the precipitated solution (shown on right).

The main objective of the current NSF award is to increase water purification membrane performance, and this work focuses on the problem of salt precipitation on the membrane surfaces from an alternative approach: concentrate treatment to reduce RO membrane fouling and to increase RO recovery. Ms. Greenlee interacted with the host laboratory in several ways during her stay. She worked closely with one of the professors, Philippe Moulin, as well as with several of the other Ph.D. students in the laboratory. A postdoc in the laboratory helped her learn how to use the laser particle counter, and Ms. Greenlee also taught several classes (a chemical engineering laboratory and an English class) to undergraduate French students. She also mentored a Masters student during his six-month internship in the laboratory. Ms. Greenlee also participated in group meetings, several local meetings and conferences, and the graduate school research colloquium.

BROADER IMPACTS OF THE INTERNATIONAL COOPERATION

The supplement award has helped to advance a female Ph.D. student in chemical engineering. Women continue to be an underrepresented group in most engineering disciplines, and women represent a minority within engineering Ph.D. students. Ms. Greenlee aspires to be a university professor and continue with her research and teaching in academia. This international experience will certainly help her achieve her goals of starting a successful research program as a junior faculty member and successfully teaching undergraduate and graduate courses. The international contacts that she has formed will be the starting point for future international collaborations and will help her secure funding for the graduate students that will work with her. In addition, Ms. Greenlee's visit to the LPPE research group in France was the first international collaboration between the research groups at The University of Texas (UT) and members of the LPPE laboratory. This successful exchange of a Ph.D. student between UT and LPPE has opened the door for future collaborations and student exchanges. The LPPE laboratory has equipment, such as several pilot-scale RO membrane units, that are not available at UT. This equipment is an importance resource for students at UT who want to scale up their research and evaluate experimental results with commercially available membrane modules.

The original scope of the NSF award was to focus on novel development of the RO membranes themselves. This supplement has significantly enhanced this scope by extending the research on RO membranes to include a specific membrane fouling process (salt precipitation) and a novel approach to reducing this type of membrane fouling (through RO concentrate treatment). With this additional research, the issues or problems found in the process of RO desalination are attacked from several different angles, and the resulting findings will help advance the knowledge and ideas of how to improve RO desalination.

The visit to France has helped Ms. Greenlee expand her knowledge of RO membrane applications and how different countries around the world use desalination to provide drinking water. Many countries have specific water problems that require different types of desalination (e.g., seawater versus brackish water, or membrane versus thermal desalination technology). Ms. Greenlee attended and gave a presentation at a meeting of the French Membrane Society and had the opportunity to interact with other researchers in both academia and industry. She discussed RO membrane desalination with researchers from France's two large water treatment companies, Veolia and Degremont. In her presentation, she explained how desalination is used in the U.S. and where water shortages exist. There are significant differences between the use of desalination in the U.S. and the use of desalination in areas such as South America and the Middle East. For example, the primary water source for desalination in the U.S. is brackish groundwater, and RO membranes are the primary technology. In comparison, commercial desalination facilities in the Middle East tend to use seawater as the feed water and several types of distillation as the desalination technology. Ms. Greenlee also learned about the need for desalination in areas such as northern Africa and China.

Ms. Greenlee also became fluent in French during her visit. All of her research, presentations during meetings, and discussions were in French and very little English was spoken. All day-to-day activities were performed in French, and she learned all of the scientific words in French related to her research and laboratory work. This type of complete immersion into the language and culture allowed her to gain an advanced understanding of the language structure and even write an article in French, as well as make presentations and teach. In addition to visiting local sights and learning about the southern France culture and habits, Ms. Greenlee traveled to Paris for several meetings, as well as Toulouse (located in southwest France). She also visited a professor (Urs von Gunten) at the Eawag, the Swiss Federal Insitute of Aquatic Science and Technology, in Zurich, Switzerland. Prof. von Gunten and his research group are internationally recognized for advancements in ozone science and technology.

DISCUSSION AND SUMMARY

This international research experience allowed a detailed investigation of Stage II (salt precipitation) of the novel concentrate treatment process. Measurements were taken for particle size distribution, dissolved ion concentration, microfiltration flux, and orthophosphate produced (during ozonation of phosphonate antiscalants). A natural water sample was tested; the sample was obtained from a karstic spring located near Marseille, France. Results showed that antiscalant degradation increases with ozonation time, as well as with ozone dose, addition of hydrogen peroxide and with the addition of carbonate. Results varied for different antiscalants tested. The addition of antiscalant to salt water caused a decrease in the particle size distribution in subsequent salt precipitation and also significantly decreased the microfiltration flux performance of Stage III. Ozonation allowed an increase in calcium precipitation, as well as an increase in the precipitated particle size distribution and a recovery of the flux performance. Therefore, ozonation (Stage I) helps to improve the performance of Stages II and III by deactivating the effect of antiscalants on the salts in solution. This RO concentrate treatment process has the potential to help increase the overall recovery of an RO membrane desalination system by removing the problematic insoluble salts and returning a large portion of the waste water volume to the membrane system. In addition to these research accomplishments, Ms. Greenlee also become fluent in French, gained future connections for international collaborations, and learned about a different culture and society.

ACKNOWLEDGEMENTS

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BRIEF BIOGRAPHY OF RESEARCHER

Lauren Greenlee received a B.S.E. in Chemical Engineering from the University of Michigan in 2001, graduating magna cum laude. During the subsequent year, she completed an internship in Basel, Switzerland, and taught English in a French high school. Greenlee then returned to the U.S. and worked for two years as an engineer for OmniGene Bioproducts, Inc., in Boston, MA, where she ran a laboratory of 7 bioreactors and 2 high pressure liquid chromatography (HPLC) machines. She started graduate school at The University of Texas at Austin (UT) in the Fall of 2004, in the Environmental and Water Resources Engineering Department (EWRE), where she won an NSF Graduate Research Fellowship in 2005 and completed a Master's degree in August 2006. She currently is pursuing her Ph.D. in Chemical Engineering at UT, under the supervision of Dr. Desmond Lawler (EWRE) and Dr. Benny Freeman (Chemical Engineering).